

Comment on "Large Difference in the Elastic Properties of fcc and hcp Hard-Sphere Crystals"

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Abstract

As is well known, hard-sphere crystals of the fcc and hcp type differ very little in their thermodynamic properties. Nonetheless, recent computer simulations by Pronk and Frenkel indicate that the elastic response to mechanical deformation of the two types of crystal should be quite different [1]. By invoking a geometrical argument put forward by R. Martin some time ago [4], we suggest that this is largely due to the different symmetries of the fcc and hcp crystal structures. Indeed, we find that elastic constants obtained by means of computer simulations for the fcc hard-sphere crystal can be mapped onto the equivalent ones of the hcp crystal to very high accuracy. The same procedure applied to density functional theoretical predictions for the elastic properties of the fcc hard-sphere crystal also produces remarkably accurate predictions for those of the hcp hard-sphere crystal.

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In a recent publication [1], Pronk and Frenkel reported on a computer simulation study of the elastic properties of fcc and hcp crystals of hard spheres. They found the various elastic constants to differ by up to twenty per cent, despite that the thermodynamic properties of both types of hard-sphere crystal are almost indistinguishable. Indeed, the free energy, pressure and compressibility of the two crystal types deviate from each other by less than 0.1%, at least for conditions not too far from the melting point [1]. In this Comment, we point out that the difference in the elasticity of fcc and hcp hard-sphere crystals is less surprising than claimed by Pronk and Frenkel, and that it can be explained by the geometry of the packing of the particles within each lattice.

The relation between the elastic moduli of hcp and fcc crystals have been studied theoretically and experimentally by number of authors. See, e.g., [2, 3, 4, 5, 6]. Of particular interest is the work of R. Martin [4], who derived an approximate transformation of the elastic moduli of the fcc crystal to those of the hcp lattice, making use of the fact that both lattice types can be constructed from tetrahedral units. The tetrahedral blocks in the fcc lattice are equally oriented, while the hcp lattice can be built up from two tetrahedra, oriented differently from each other and from those of the fcc lattice. The transformation of any tensor in the fcc system of coordinates (defined as usual along the cubic axes) to either of the two representations of this tensor in the trigonal geometry of the hcp crystal can be made by two simple rotations $\mathbf{R}^{(1)}$ and $\mathbf{R}^{(2)}$, where

$$\mathbf{R}^{(1)} = \begin{pmatrix} \sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} \\ -\sqrt{\frac{1}{6}} & \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{6}} \\ -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \end{pmatrix}, \quad \mathbf{R}^{(2)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \mathbf{R}^{(1)}. \quad (1)$$

This suggests that the transformation of the elastic moduli tensor in the fcc geometry, \mathbf{C}^{FCC} , to that of the trigonal geometry of the hcp lattice, $\overline{\mathbf{C}}^{HCP}$, could simply be the average (superposition) of the two trigonal tensors [6],

$$\overline{C}_{ijkl}^{HCP} = \frac{1}{2} \left(R_{ir}^{(1)} R_{js}^{(1)} R_{kt}^{(1)} R_{lu}^{(1)} C_{rstu}^{FCC} + R_{ir}^{(2)} R_{js}^{(2)} R_{kt}^{(2)} R_{lu}^{(2)} C_{rstu}^{FCC} \right), \quad (2)$$

where the subscripts have their usual meaning. It so happens, however, that the two unequal tetrahedra of the hcp lattice are not independent, but attached to each other. Hence, the elastic response of the hcp lattice to an external strain should be the *combined* response of both tetrahedra, not just a simple average, implying that Eq. (2) requires a correction for the internal strain that the connectedness of and interaction between the tetrahedra

produce. We refer to ref. [4] for further details. The resulting strain-corrected expression for the elastic moduli tensor of the hcp lattice, \mathbf{C}^{HCP} , reads [4]

$$C_{ijkl}^{HCP} = \overline{C}_{ijkl}^{HCP} - \Delta_{ijrs} (\overline{C}_{rstu}^{HCP})^{-1} \Delta_{tukl}, \quad (3)$$

where \overline{C}^{HCP} is given by Eq. (2) and Δ is a correction tensor identical to it, except that the difference between the two components is taken instead of the sum.

There are six distinct elastic moduli in the trigonal representation of which only three are independent in the fcc crystal and five in the hcp crystal. The relations between the elastic moduli of the fcc lattice and those of the hcp lattice *not* corrected for the internal strain are given by (using standard Voigt notation)

$$\begin{aligned} \overline{C}_{11}^{HCP} &= (C_{11}^{FCC} + C_{12}^{FCC} + 2C_{44}^{FCC})/2, \\ \overline{C}_{12}^{HCP} &= (C_{11}^{FCC} + 5C_{12}^{FCC} - 2C_{44}^{FCC})/6, \\ \overline{C}_{13}^{HCP} &= (C_{11}^{FCC} + 2C_{12}^{FCC} - 2C_{44}^{FCC})/3, \\ \overline{C}_{14}^{HCP} &= (C_{11}^{FCC} - C_{12}^{FCC} - 2C_{44}^{FCC})/3\sqrt{2}, \\ \overline{C}_{33}^{HCP} &= (C_{11}^{FCC} + 2C_{12}^{FCC} + 4C_{44}^{FCC})/3, \\ \overline{C}_{44}^{HCP} &= (C_{11}^{FCC} - C_{12}^{FCC} + C_{44}^{FCC})/3. \end{aligned} \quad (4)$$

The strain-corrected constants obey

$$\begin{aligned} C_{11}^{HCP} &= \overline{C}_{11}^{HCP} - (\overline{C}_{14}^{HCP})^2 / \overline{C}_{44}^{HCP}, \\ C_{12}^{HCP} &= \overline{C}_{12}^{HCP} + (\overline{C}_{14}^{HCP})^2 / \overline{C}_{44}^{HCP}, \\ C_{13}^{HCP} &= \overline{C}_{13}^{HCP}, \\ C_{14}^{HCP} &\equiv 0, \\ C_{33}^{HCP} &= \overline{C}_{33}^{HCP}, \\ C_{44}^{HCP} &= \overline{C}_{44}^{HCP} + (\overline{C}_{14}^{HCP})^2 / [\frac{1}{2}(\overline{C}_{11}^{HCP} - \overline{C}_{12}^{HCP})]. \end{aligned} \quad (5)$$

The mapping of \mathbf{C}^{FCC} onto \mathbf{C}^{HCP} implicit in Eqs. (4) and (5) agrees well with experimental data on ZnS, a compound that can crystallize both in an fcc and in an hcp lattice [4]. In fact, the mapping works very well for fcc and hcp crystals of hard spheres too, as we show next.

In Figure 1, we have plotted the relative difference between the various moduli of the fcc and hcp crystals of hard spheres as a function of the dimensionless crystal density $\rho_S \sigma^3$, with

ρ_s the number density and σ the diameter of the spheres, using the computer simulation data of Pronk and Frenkel (obtained from Table I of Ref. [1]) and the prediction of Martin, Eqs. (1–5) [4]. We find that the largest deviation between the two is about 6%. This implies that the approximate theory outlined above, based entirely on a geometric argument, plausibly explains the difference between the elastic moduli of fcc and hcp crystals. That is, geometry explains almost all of the found differences in elastic behavior of fcc and hcp crystals.

In order to further verify Eqs. (1–5), we calculated the elastic moduli of the hcp hard-sphere crystal, using results for the elastic moduli of fcc crystals of hard spheres obtained from density functional theory (DFT) [7]. We used the predictions of the modified weighted-density approximation DFT, MWDA DFT, because they are known to agree very well with the results of computer simulations. The results of the mapping of the fcc moduli onto the hcp moduli are presented in Figure 2, again as a function of the dimensionless density of the spheres. The agreement with the results of the computer simulations of Pronk and Frenkel is quite good for all moduli except C_{13} , for which it is not as impressive but still satisfactory.

We believe to have demonstrated that the large difference in elasticity between the fcc and hcp crystals of hard spheres found in [1] is largely caused by the geometrical differences of these two types of crystal lattice. We point out that even when the thermodynamic properties of fcc and hcp crystals are similar to the point of being virtually indistinguishable, there is in fact no reason for their elastic properties to be similar too. The reason is that similarities in the free energy landscape at long wavelengths do not preclude differences at short wavelengths. Indeed, (direct) correlations at short wavelengths contribute much more significantly to the elastic constants than to the equilibrium free energy [8].

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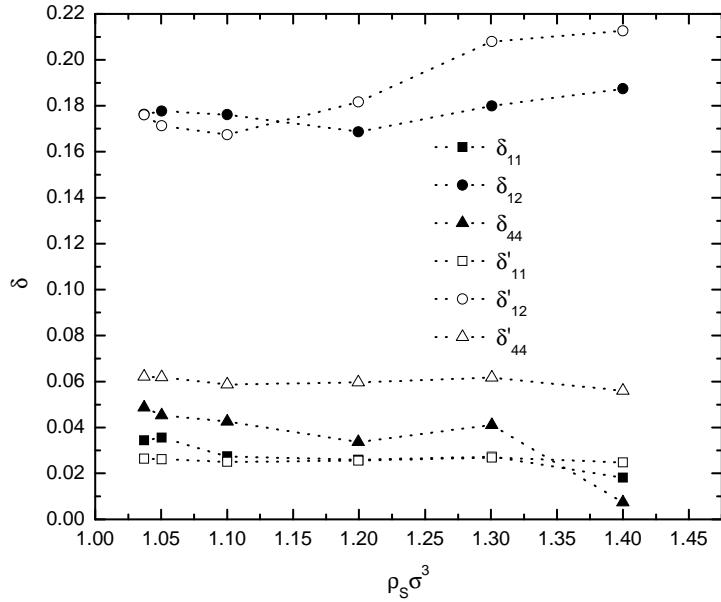


FIG. 1: Relative difference $\delta_{ij} \equiv |C_{ij}^{FCC} - C_{ij}^{HCP}|/C_{ij}^{FCC}$ between the elastic moduli of the hcp and fcc crystals, as a function of the dimensionless density $\rho_S\sigma^3$. Shown are the results of computer simulations of Ref. [1], δ_{ij} , and the ones computed using relations Eqs. (1–5), δ'_{ij} .

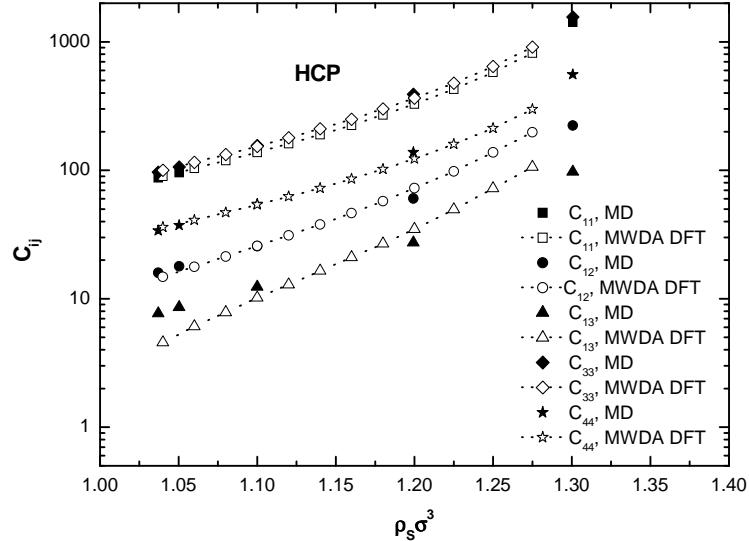


FIG. 2: The dimensionless elastic moduli $C_{ij} \equiv C_{ij}\sigma^3/k_B T$ of the hcp crystal computed using the relations Eqs. (1–5) and the results of the MWDA DFT calculations for the fcc crystal [7], as a function of the dimensionless crystal density $\rho_S\sigma^3$. Also shown are the results of the computer simulations of Ref. [1].